

Re-evaluation of the Cation Distribution in Orthopyroxenes by the
Mössbauer Effect

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Abstract

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The resolution of Mössbauer spectra of orthopyroxenes is improved by measurement of the absorbers at temperatures close to liquid nitrogen. Some previously published data on the ferrous ion distribution between M_1 and M_2 have been reevaluated.

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The hyperfine splitting of Fe^{57} observed by Mossbauer resonance absorption has been recently used¹⁻⁵ to investigate the distribution of Fe^{2+} over the two non-equivalent lattice sites M_1 and M_2 in orthopyroxenes (minerals close to the system $\text{FeSiO}_3\text{-MgSiO}_3$). Orthopyroxene spectra consist of two distinct doublets arising from the nuclear quadrupole interaction of Fe^{57} at M_1 and M_2 . As a measure of the Fe^{2+} distribution, the intensity ratio of the doublets has been used from spectra taken at room temperature, and Fe^{2+} site occupancy factors for M_1 and M_2 have been derived. However, there is a discrepancy in the data published by different groups on orthopyroxenes which are expected to exhibit similar results. While e.g. Bancroft, Burns, and Howie¹ found that orthopyroxenes from metamorphic rocks (specimens 68671, 355 and K23) are considerably disordered with respect to Fe-Mg at M_2 and M_1 , Evans, Ghose, and Hafner⁴ quote site occupancy factors which indicate substantial ordering for samples with similar $\text{Fe}/(\text{Fe}+\text{Mg})$ ratios. The inconsistencies appear to be primarily due to the poor resolution of the two overlapping doublets at room temperature and to differences in the individual techniques used to fit Lorentzian curves to the absorption spectra.

We have overcome this problem of poor resolution by carrying out experiments with the absorbers held at temperatures close to liquid nitrogen. Resolution is strikingly improved due to a differential increase of the quadrupole splitting at M_1 and M_2 . Measurements of the relative intensities of the doublets using this technique have revealed

large discrepancies with already published results, and we feel that revision of some of the room-temperature data will be necessary. Sprenkel-Segel and Perlow^{6,7} have taken spectra at 77°K of chondritic meteorites which include pyroxenes as silicate phases. From a spectrum of the Johnstown meteorite which contains orthopyroxene ($\text{Fe}/(\text{Fe}+\text{Mg}) = 0.24$) but no detectable olivine, they found⁷ that 6 percent of Fe^{2+} is located at M_1 . This value is in surprisingly good agreement with the assumption of a simple, ideal solution model at each site for metamorphic samples of the orthopyroxene system⁵.

The samples discussed in this paper include two of the metamorphic orthopyroxenes investigated by Bancroft, Burns and Howie^{1,8} ($\text{Fe}/(\text{Fe}+\text{Mg}) = 0.531$ and 0.775), a natural and heated metamorphic sample discussed by Evans Ghose and Hafner⁴ ($\text{Fe}/(\text{Fe}+\text{Mg}) = 0.532$), a natural and heated igneous orthopyroxene⁹ ($\text{Fe}/(\text{Fe}+\text{Mg}) = 0.269$), and a synthetic orthopyroxene¹⁰ ($\text{Fe}/(\text{Fe}+\text{Mg}) = 0.80$). A Co^{57} source diffused into Pd was used. The absorbers were prepared by mixing 0.5 gr. lucite with 60-80 mgr. of powdered mineral and pressing the mixture to a pellet. The mass of natural ferrous ion per unit area varied from 3.1-4.6 mgr. Fe/cm^2 . No correction for saturation (thickness) was made. The spectra were fitted by Lorentzians without using any constraints. The halfwidths of the peaks (full widths at half intensity) were found to be ~ 0.30 mm/sec at 77°K. For further details about experiment and spectral analysis, the reader is referred to ref. 4.

It is known that the intensities of the left and right peaks of the orthopyroxene doublets are generally not symmetric⁴. Employing the same notation as previously⁵, the relative intensities of the two doublets are $(A_1+B_1)/(A_1+B_1+A_2+B_2)$ and $(A_2+B_2)/(A_1+B_1+A_2+B_2)$, respectively. As measure of the intensities, the areas of the fitted Lorentzians (product of halfwidth and maximum intensity) were taken.

Plots (Fig. 1-3) of some of these samples at 77°K compared with the room-temperature spectra illustrate the improved resolution of Fe^{2+} at the two sites. Also, Figs. 2b and d and Figs. 3a and b demonstrate the exchange of Fe^{2+} and Mg between sites by heating a natural orthopyroxene at 1000°C for 7 days. With increasing temperature, the ferrous ion concentration increases at the M_1 sites (outer peaks in Figs. 2b,d and 3a,b) at the expense of the magnesium concentration. Fig. 3a shows a limit to the resolution obtained for a highly ordered Mg rich orthopyroxene ($\text{Fe}/(\text{Fe}+\text{Mg}) = 0.269$). However, the spectrum of this specimen heat treated at 1000°C for 7 days, clearly exhibits the presence of divalent iron at both sites (Fig. 3b).

Tables 1 and 2 exhibit site occupancy factors of the ferrous ion calculated from the Fe distribution between the sites according to the method used by Bancroft, Burns, and Howie¹ (Tb. 1), and also that used by Evans, Ghose and Hafner^{4,5} (Tb. 2). Using either of these methods, it is apparent that deviations exist between the results at 77°K and the values derived from room-temperature spectra (cf. Tb. 1). We believe that these errors must be attributed to the individual computer fitting technique when applied to unresolved or poorly resolved absorption peaks.

The distinction between the doublets at M_1 and M_2 depends on the Fe/Mg ratio of the orthopyroxene⁴. Only for compositions very rich in iron ($\text{Fe}/(\text{Fe}+\text{Mg}) > 0.75$) can the room-temperature spectrum be reliably fitted without constraints. For ratios $\text{Fe}/(\text{Fe}+\text{Mg}) < 0.75$, Evans et al.⁴ introduced constraints for half widths and positions of the doublets in their least squares analysis. We believe that using constraints for strongly overlapping peaks is a rather involved problem, and possible error sources were discussed in detail by

these authors. The agreement between the two sets of data in Table 2 is probably accidental. Alternatively, Bancroft et al.¹ fitted orthopyroxene spectra with Fe/(Fe+Mg) ratios of about 0.5 without any constraints. Some of their samples reported to be considerably disordered turn out to be nearly ordered (Tb. 1).

There are additional inconsistencies between the data of Tables 1 and 2. Firstly, Bancroft et al.¹ used a constant $C = 0.9$ to account for the non-equivalent recoilless fraction of Fe^{57} at M_1 and M_2 while Evans et al. assume that the recoilless fraction is the same at both sites. We carefully studied the spectrum of orthoferrosilite¹⁰ (FeSiO_3) and found that the recoilless fraction is in fact very nearly the same ($C = 1.0 \pm 0.1$). In addition, if a differential recoilless fraction existed at M_1 and M_2 , C is expected to be dependent on the temperature. This was not observed. For this reason, $C = 1$ was used in Table 2 as previously. In Table 1, last column, C was set $C = 0.9$ to provide the proper basis for comparison with data of columns 4 and 5.

Secondly, there is an ambiguity in deriving the Fe^{2+} site occupancy factors of M_1 and M_2 from the Fe^{2+} distribution. We have calculated these factors by multiplication of the intensity ratio of the M_1 and M_2 doublets by the total ratio of $2 \text{ Fe}/(\text{Fe}+\text{Mg})$ of the mineral according to two formula units per unit cell. Other groups^{1,2} preferred to derive the factors from the product of the intensity ratio of the M_1 and M_2 doublets and the cation percent Fe^{2+} , calculated on the basis of 6 oxygen atoms per formula unit. These two techniques result in site occupancy factors which differ by a few percent.

While the 77°K spectra demonstrate the potential of the Mossbauer

method to determine the iron distribution very accurately, possibly with a precision of a fraction of one percent, the data reported in this note are still regarded as preliminary. We hesitate to assign appropriate error estimates at this time. A detailed error analysis and an investigation of the hyperfine parameters as function of the degree of Fe/Mg order will be submitted elsewhere.

Finally, it is to be noted that measurements of orthopyroxene spectra between 77°K and 1.7°K do not lead to a further improvement of the resolution of the overlapping doublets. At temperatures below 77°K, the spectra are complicated by relaxation effects¹².

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10. We are indebted to Professor S.I. Akimoto from the University of Tokyo for the synthesis of samples.
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Figure captions

Figure 1. a) Spectrum of orthopyroxenes ($\text{Fe}/(\text{Fe}+\text{Mg}) = 0.80$) synthesized at 1200°C , 45 K bars for 40 minutes¹⁰ and measured at room temperature.

b) Same sample measured at 77°K . The solid lines are the Lorentzian fits.

Figure 2. a) Spectrum of natural orthopyroxenes 37218 ($\text{Fe}/(\text{Fe}+\text{Mg}) = 0.532$) measured at room temperature. (Fig. 5 of ref. 4).

b) Same sample measured at 77°K . The solid lines are the Lorentzian fits.

c) Spectrum of orthopyroxene 37a18 ($\text{Fe}/(\text{Fe}+\text{Mg}) = 0.532$) heated at 1000°C for 7 days and measured at room temperature. (Fig. 7 of ref. 4).

d) Same sample measured at 77°K . The solid lines are the Lorentzian fits.

Figure 3. a) Spectrum of natural orthopyroxene N-5 ($\text{Fe}/(\text{Fe}+\text{Mg}) = 0.269$ ⁹) measured at 77°K . The solid lines are the Lorentzian fits.

b) Same sample heated at 1000°C for 7 days and measured at 77°K . The solid lines are the Lorentzian fits.

Table 1.

Ferrous Ion Distribution in Orthopyroxenes (samples initially reported by Bancroft et al.¹)

Specimen	Fe/(Fe+Mg) (at. prop.)	Fe ²⁺ per formula unit	Site occupancy factors			
			Previously published data ^a (room temperature)		This work ^b (77°K)	
			M ₁	M ₂	M ₁	M ₂
68671	0.531	0.968	0.25	0.72	0.14	0.83
355 ^c	0.775	1.454	0.66	0.79	0.51	0.94

^aBancroft et al.¹.

^bCalculated according to the method used by Bancroft et al.¹.

^cThis sample is not numbered as such in Bancroft et al.¹ (Table 1) but the identity of this sample has been determined by its chemical analysis given in Howie¹¹.

Table 2.

Ferrous Ion Distribution in Orthopyroxenes (samples initially reported by Evans et al.⁴).

Specimen	Fe/(Fe+Mg) (at. prop.)	Fe ²⁺ per formula unit	Site occupancy factors ^a	
			Previously published data (room temperature)	This work (77°K)
			M ₁ M ₂	M ₁ M ₂
37218 (natural)	0.532	1.00	0.16 0.91	0.17 0.90
37218 (heated at 1000° for 7 days)	0.532	1.00	0.29 0.78	0.29 0.77

^aCalculated according to method used by Ghose and Hafner⁵.

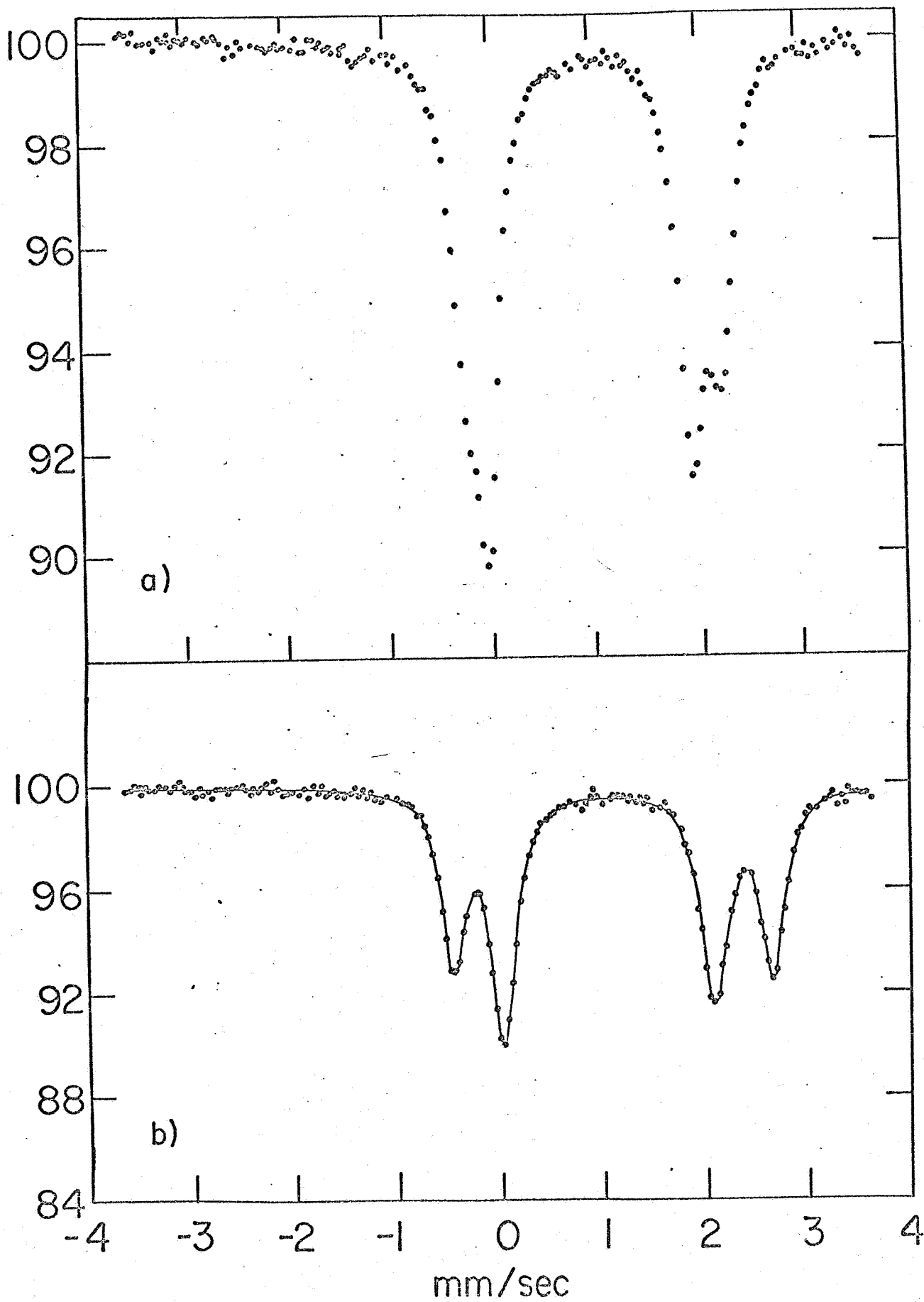
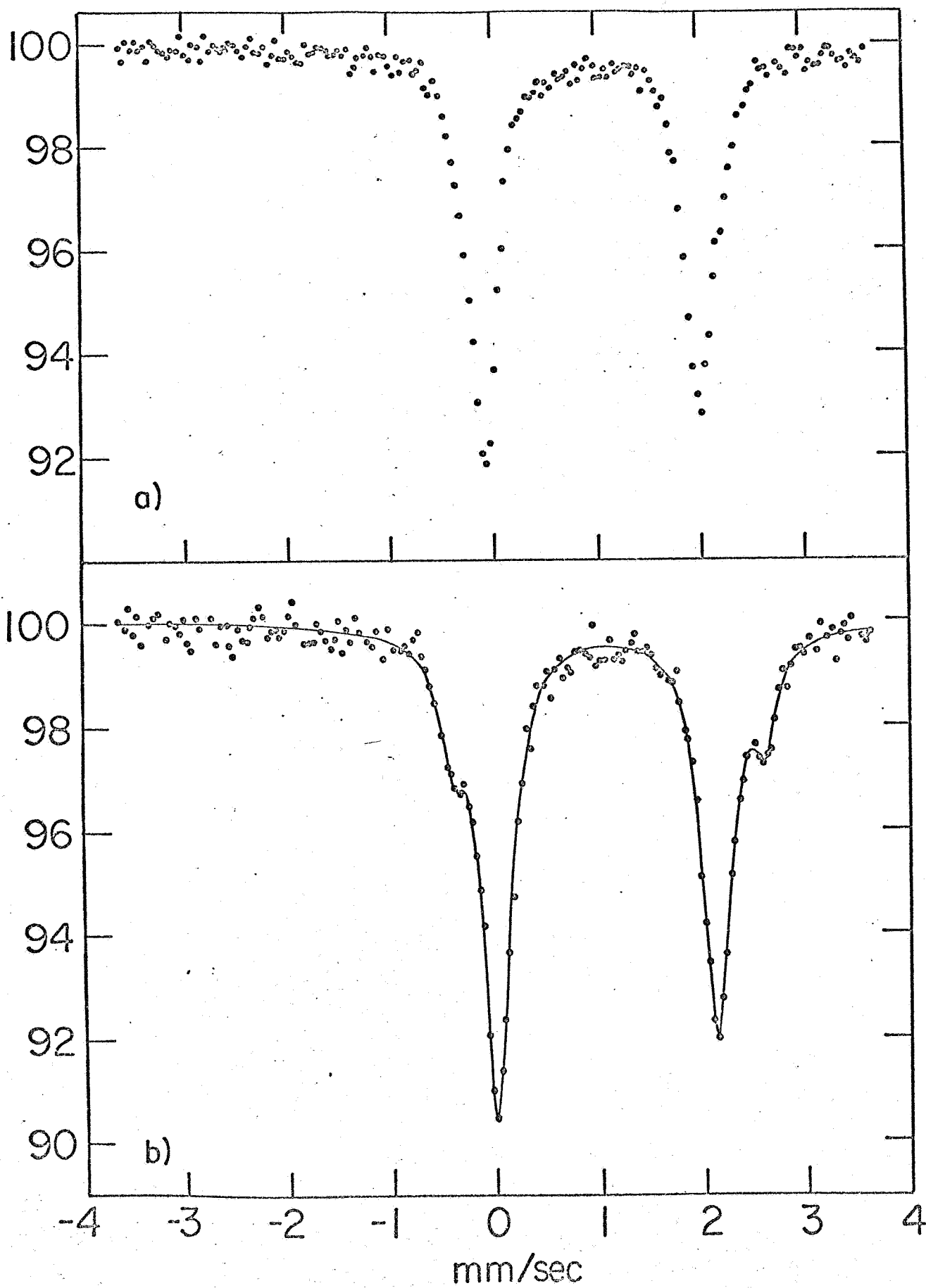


Figure 2a, 2b



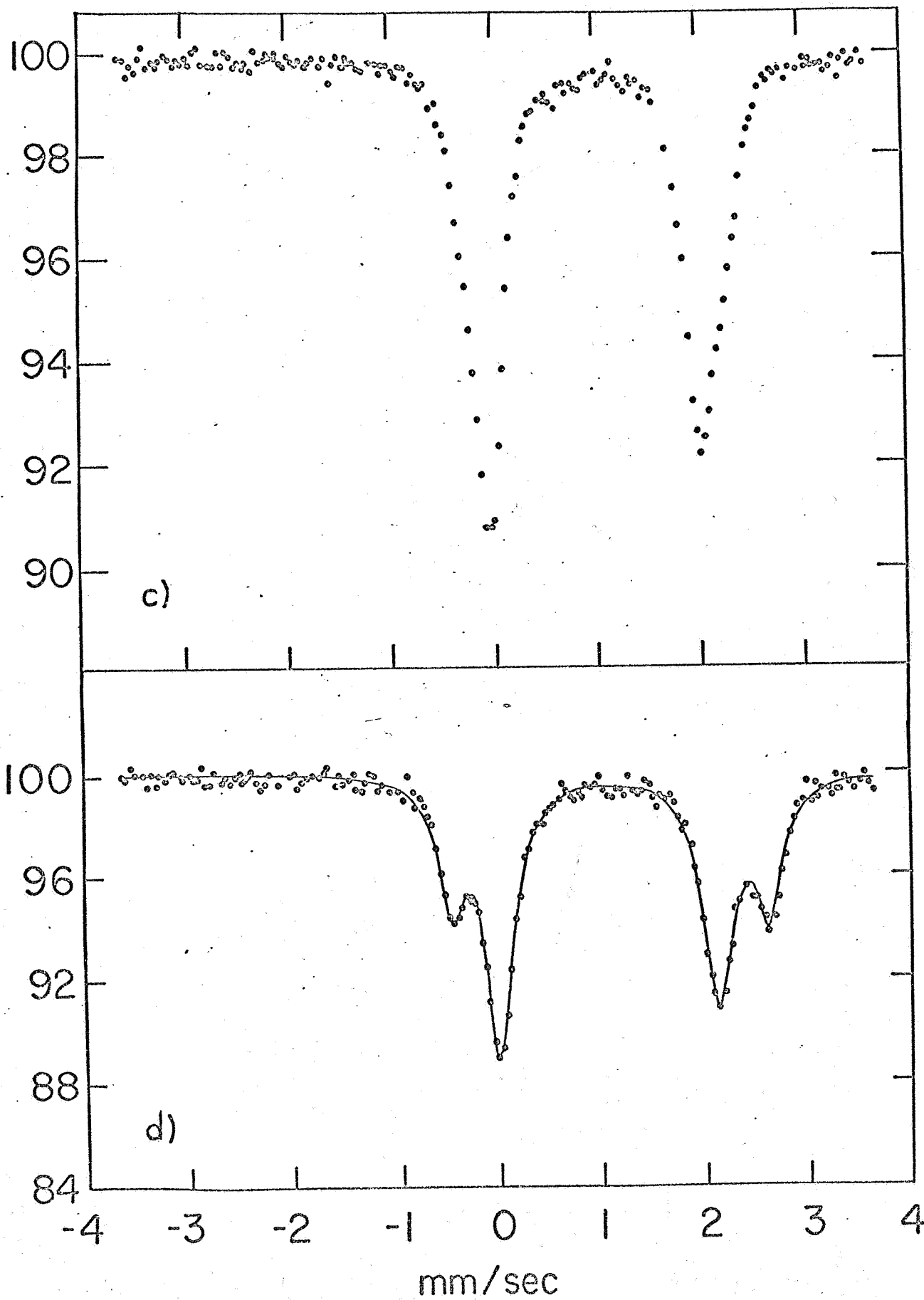


Figure 30-20

